Superconductivity in heavily vacant diamond

M. Alaei[1], S. Akbar Jafari[1] and H. Akbarzadeh[1]

[1]*Department of Physics, Isfahan University of Technology, Isfahan 84156-83111, Iran*

(Dated: July 30, 2008)

Using first principle electronic structure calculations we investigated the role of substitutional doping of B,N,P,Al and vacancies ($\mathcal{V}$) in diamond ($X_\alpha C_{1-\alpha}$). In the heavy doping regime, at about $\sim 1 - 6\%$ doping an impurity band appears in the mid gap. Increasing further the concentration of the impurity substitution fills in the gap of the diamond host. Our first principle calculation indicates that in the case of vacancies, a clear single-band picture can be employed to write down an effective *one band* microscopic Hamiltonian, which can be used to further study various many-body and disorder effects in impurity band (super)conductors.

I. INTRODUCTION

Diamond has a number of unique attributes that make it highly suited as a gem stone. It is the hardest known material which can only be scratched by another diamond. The thermal conductivity of diamond is the highest among all materials [1, 2]. Irradiation of diamond by various particles (e.g. electrons, neutrons, α particles) followed by annealing to repair damaged sp^3 bonds gives rise to fascinating colours of diamond, which are due to the so called colour centers [3].

Diamond is also a material with semiconductor properties that are superior to Si, Ge, or GaAs, which are now commonly used. The use of diamond in electronic applications is not a new idea, but limitations in size and control of properties restricted the use of diamond to a few specialized applications. The vapor-phase synthesis of diamond, however, has facilitated serious interest in the development of diamond-based electronic devices. The process allows diamond films to be laid down over large areas. Both intrinsic and doped diamond films have a unique combination of extreme properties for high speed, high power and high temperature applications [2, 4, 5].

Ekimov and coworkers [7] and subsequently Takano *et. al.* [8] used chemical vapor deposition (CVD) to synthesized B-doped diamond. Doping diamond by low concentration of typically $10^{17} - 10^{18}$ cm^{-3} boron atoms gives rise to acceptor level, rendering it to a p type semiconductor [6]. Increasing the doping level to [B]/[C]> 5000 ppm in the gas phase induces metallic conductivity in diamond [9]. Further increasing the doping rate to the scale of $n > 10^{21}$ cm^{-3}, i.e. $\sim$ few %, makes it superconduct at low temperatures [7, 8]. Increasing the doping rate amounts to bringing the boron atoms closer, and allow them to overlap more effectively, which broadens the acceptor levels in to decent bands of electrons [10, 11], which are responsible for metallic and superconducting properties [11, 12, 13, 14, 15, 16, 17].

Also some authors have investigated the doping of silicon with boron, aluminum and phosphorus [18, 19]. Experiment has showed that the transition temperature for B-doped Si is $T_c \sim 0.35$ K. Therefore doping C with boron gives more than an order of magnitude larger $T_c \sim 4$ K compared to B doped Si. Hence we choose the host material to be carbon rather than any other element in the same group.

Now the question arises, what other elements can be doped into diamond in the regime of heavy ($\sim 1 - 10\%$) doping which can possibly lead to higher superconducting T_c. In the example of high temperature cuprate superconductors (HTSC) [20], an effective one-band model for the so called Zhang-Rice singlet [21] can be written down in terms of the hole states of the O2p and Cu3d. In $X_\alpha C_{1-\alpha}$ case also the effective impurity band has a mixed Xnp and C2p character. Here $n = 2$ for X=B,N and $n = 3$ for X=Al,P. In the case of X=$\mathcal{V}$ the picture is even simpler. The metallic band in the middle of the diamond gap well isolated from both bands is almost entirely due to the nearest neighbor C atoms surrounding the vacant site. In this work we present our preliminary result on comparison of the impurity band formation for the above elements for various doping rates $\alpha = 1/128, 1/54, 1/16$.

II. METHOD OF CALCULATION

In this study we used the Plane Wave-Pseudopotential Quantum-ESPRESSO code [22]. We used Density Functional Theory with General Gradient Approximation (GGA). The GGA exchange-correlation functional which has been used is PBE [23]. We employed ultrasoft pseudopotential [24] to describe electron-ion interaction. The energy cutoff for expansion of wave function in plane wave was 25 Ry, and 150 Ry has been used for expansion of charge density. We chose $2 \times 2 \times 2$, $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercell with one vacancy or with a defect, that is $X_\alpha C_{1-\alpha}$ with $\alpha = 1/128, 1/54, 1/16$. B, N, Al, P are chosen to substitutionally replace one carbon atom in a diamond structure. The k-point is sampled according to table I. To accelerate electronic structure calculation, we use Methfessel and Paxtons Fermi-level smearing method (width 0.01 Ry) [25]. The impurity has been only substituted by one of carbon atom in diamond structure without any relaxation.

TABLE I: The k-point sampling for different supercells.

Supercell	k-point grid	number of atomic sites
$2 \times 2 \times 2$	$6 \times 6 \times 6$	16
$3 \times 3 \times 3$	$4 \times 4 \times 4$	54
$4 \times 4 \times 4$	$3 \times 3 \times 3$	128
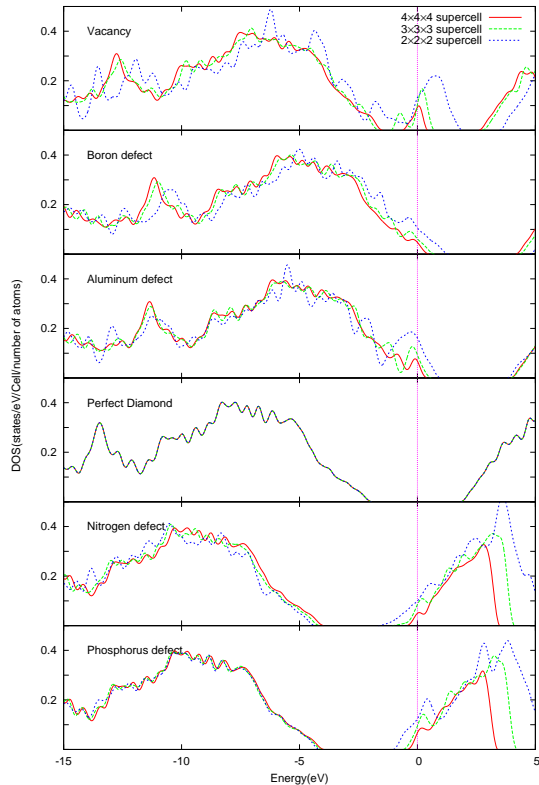
FIG. 1: The density of state (DOS) for various concentrations of B, Al, N, P and $\mathcal{V}$ impurities in diamond.

III. RESULTS AND DISCUSSION

The results of this work has been summarized in Fig. 1 where we have plotted the density of state (DOS) for various impurities and different impurity concentrations. We have shifted the data such that the Fermi level in all cases is at $E_F = 0$. The impurity band formation for the vacancy and Aluminum are the most clear among the cases studied here. Their bandwidths are between 1.5 eV to 0.5 eV for different impurity concentration.

For the perfect diamond lattice the DOS for all sizes of the unit cell coincide and give the clean diamond gap. However substitutional doping with B and Al starts to create acceptor levels on top of the valence band which broaden into bands in the regime of few percent impurity concentration. Also in this regime the relevant orbitals of

the impurity atoms will hybridize with the C2p orbitals, and the impurity band has a mixed character, similar to the case of Zhang-Rice singlet of cuprates [21]. It is clearly seen that the impurity band peak in the case of Al is stronger than B. Also the value of the DOS at the Fermi level (ρ_0) is larger for Al doping than B doping. N and P similarly create donor levels at the buttom of the conduction band. Again qualitatively one can see that P tends to give a sharper impurity band peak than the N. Here also the impurity band arises from a combination of nearest neighbor C2p and N2p or P3p bands.

In the case of vacancy, the story is different. First of all, since $\mathcal{V}$ is neither acceptor, nor donor level, the resulting band will be in the middle of the gap, well isolated from the valence and conduction band. Secondly the impurity band arises from the n.n. carbon atoms surrounding the vacancy. This qualitative picture can be inferred by looking at the orbital and site resolved partial DOS (not shown here). Therefore for the effective one band model of the impurities proposed by Baskaran [11], doping by $\mathcal{V}$ seems to be more suitable than the other cases studied in this investigation.

Note that in this study we have ignored issues like the formation of various complexes. For example, nitrogen doping in diamond usually leads to the formation of nitrogen-vacancy complex [26]. Ignoring such complications, one can use the argument of Mott to get a rough estimate of the typical density needed to make the the resulting half-filled impurity band superconduct: The critical concentration needed for metalization is given by $a_B^3 n_c = 1/4$, where the Bohr radius a_B of the impurity can be estimated from the binding energy E_B of the impurity levels as $a_B = \frac{e^2}{2\varepsilon_0 E_B}$. For typically $0.5 - 1.5$ eV binding energies of say, Al, $\mathcal{V}$, the Bohr radius will be $1-3$ atomic units, giving a critical concentration on the scale of $\sim 10^{21}$ cm^{-1} or $5-15$ percents. For the concentrations affordable in our calculations, at $\alpha = 1/16 \approx 6\%$ non of the impurities studied here fills in the gap. However Cu doping at nearly 6% already metalizes the diamond [27].

According to a disordered RVB mechanism suggested by Baskaran [11], for such an effective single band at half filling the critical temperature for the superconductivity is given by $k_B T_c \approx \frac{W}{2} e^{\frac{-1}{\rho_0 J}}$, where J is superexchange, W the band width, and ρ_0 is the DOS at the Fermi level obtained from the DFT bands. The effective one band model must have large enough W to escape the Mott-Hubbard splitting in the large U limit, such that the half-filled band picture remains valid. Also the disordered nature of the impurity centers will start to localize the states close to the impurity band edges. Again the bandwidth W must be wide enough such that the mobility edge will not cross the Fermi level.

If one assumes that the superconducting mechanism remains the same for various impurities X studied here, vacancy and Al doping offer a more clear picture of the half-filled band undergoing Anderson-Mott to RVB superconducting scenario of Baskaran [11]. The enhancement of ρ_0 observed for the case of similar concentration

of Al and $\mathcal{V}$ is advantageous in giving larger transition temperature than the case of Boron. Note that larger ρ_0 even within the BCS picture is an advantage of $\mathcal{V}$ and Al doping compared to doping by B.

In terms of practical fabrication, utilizing the heavily vacant diamond may offer a new method in addition to high temperature high pressure techniques used in production of CVD diamond doped with various elements. Irradiation by different particles may offer a method of producing high concentration of vacancies in diamond which can possibly lead to higher transition temperature than the CVD diamond doped with elements.

IV. ACKNOWLEDGMENTS

[1] Field, J.E., *The Properties of Natural and Synthetic Diamond*, Academic Press, 1992.
[2] Davies, G. (Ed.) *Properties and Growth of Diamond*, IN-SPEC, 1994.
[3] A.T. Collins in: *The Physics of Diamond*, IOS Press, 1997, Edited by A. Paoletti, and A. Tucciarone.
[4] Nebel, C.E., and J. Ristein, *Thin-Film Diamond I*, Elsevier, 2003.
[5] Lowrence S. Pan, Don R. Kania *Diamond electronic properties and applications*, Springer, 1994.
[6] R. Kalish in: *The Physics of Diamond*, IOS Press, 1997, Edited by A. Paoletti, and A. Tucciarone.
[7] E.A. Ekimov, V.A. Sidorov, E.D. Bauer, N. N. Melnik, N.J. Curro, J.D. Thompson, and S.M. Stishov: Nature (London) **428** (2004) 542.
[8] Y. Takano, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, K. Kobayashi, H. Umezawa, and H. Kawarada: Appl. Phys. Lett. **85** (2004) 2851.
[9] A. Deneuville in: *The Physics of Diamond*, IOS Press, 1997, Edited by A. Paoletti, and A. Tucciarone.
[10] Dan Wu, *et. al.*, Phys. Rev. B **73** (2006) 012501.
[11] G. Baskaran, Sci. Technol. Adv. Mat. **7** (2007) S49-S53.
[12] K.-W. Lee, and W.E. Pickett, Phys. Rev. Lett. **93** (2004) 237003; Phys. Rev. B **73** (2006) 075105.
[13] Yu.G. Pogorelov, V.M. Loktev, Phys. Rev. B **72** (2005) 075213.
[14] J. Nakamura, *et. al.*, Phys. Rev. B **70** (2004) 245111.
[15] X. Blase, C. Adessi, D. Connetable, Phys. Rev. Lett. **93** (2004) 237004.
[16] H. Mukuda *et. al.*, Phys. Rev. B **75** (2007) 033301.
[17] T. Shirakawa, S. Horiuchi, H. Fukuyama, J. Phys. Soc. Jpn. **76** (2007) 014711.
[18] E. Bourgeois, X. Blase, App. Phys. Lett. **90** (2007) 142511.
[19] E. Bustarret *et. al.*, Nature (London) **444** (2006) 465.
[20] P.W. Anderson, *The theory of superconductivity in the hight-Tc cuprates*, Princeton University Press, 1997.
[21] F.C. Zhang, and T.M. Rice, Phys. Rev. B **37** (1988) 3759.
[22] www.pwscf.org
[23] Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. **77**, 3865 (1996).
[24] Vanderbilt D., Phys. Rev. B **41**, 7892 (1990).
[25] Methfessel, M.; Paxton, A. T. Phys. Rev. B **40**, 3616 (1989).
[26] A. Mainwood, J. Mater Sci: Mater Electron **17** (2006) 453-458.
[27] H. Hassanian Arefi, S.A. Jafari, and M.R. Abolhasani, unpublished.